Facile Synthesis of 2-(2-Ethoxy-1,2-dioxoethyl)azoles

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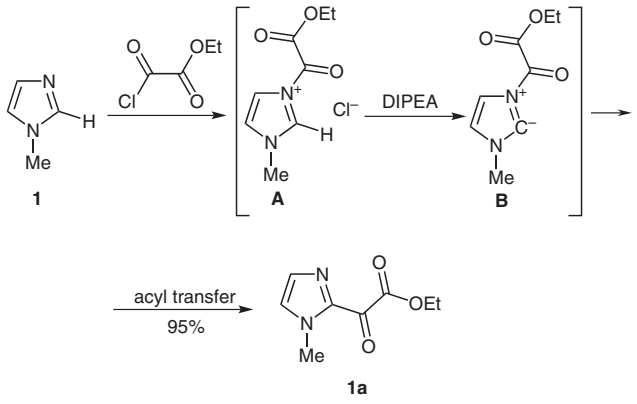
Abstract: C-Acylation of N-substituted imidazoles with ethyl oxalyl chloride in the presence of *N*,*N*-diisopropylethylamine as a base afforded 2-(2-ethoxy-1,2-dioxoethyl)imidazoles in 83–95% yield. Application of this synthetic protocol to thiazoles and triazoles led to the corresponding 2-ethoxy-1,2-dioxoethyl derivatives in 40–51% yield.

Key words: azoles, acylations, glyoxylates, keto esters, heterocycles

α-Keto acids and their derivatives are very abundant within drug discovery programs.[1] The antineoplastics indibulin[2] and rosabulin,[3] the antithrombotic tiplasinin,[4] the septic shock agent varespladib,[5] and the anti-Alzheimer's disease agent aleplasinin[6] are representative examples of pharmacologically relevant heterocyclic derivatives of α-keto acids (Figure 1). In this context, the development of novel synthetic methodologies for the practical preparation of functionalized α-keto acid precursors is of particular interest. Herein, we report a facile one-step procedure for the synthesis of 2-(2-ethoxy-1,2-dioxoethyl)azoles.

Despite the great potential of the imidazole motif in medicinal chemistry,[7] there are only a few isolated examples reported in the literature on the preparation of 2-(imidazolyl)-2-oxoacetates from N-substituted imidazoles and oxalic acid derivatives.[8] A systematic study of this transformation, has, however, not been performed.

N-methylimidazole (**1**) was chosen as the model compound in this study (Scheme 1). Addition of ethyl oxalyl chloride to a solution of compound **1** in anhydrous dichloromethane at –20 °C led to the formation of a precipitate, which presumably had the structure of ionic compound **A**. Subsequent addition of the base *N*,*N*-diisopropylethylamine to the reaction mixture resulted in dissolution of the precipitate and formation of a transparent solution. After 12 hours of stirring at room temperature, standard workup of the reaction mixture afforded the target product **1a** in an excellent yield of 95% (Scheme 1, Table 1). Deprotonation of intermediate **A** by *N*,*N*-diisopropylethylamine



Scheme 1 Acylation of *N*-methylimidazole (**1**) with ethyl oxalyl chloride in the presence of *N*,*N*-diisopropylethylamine as a base

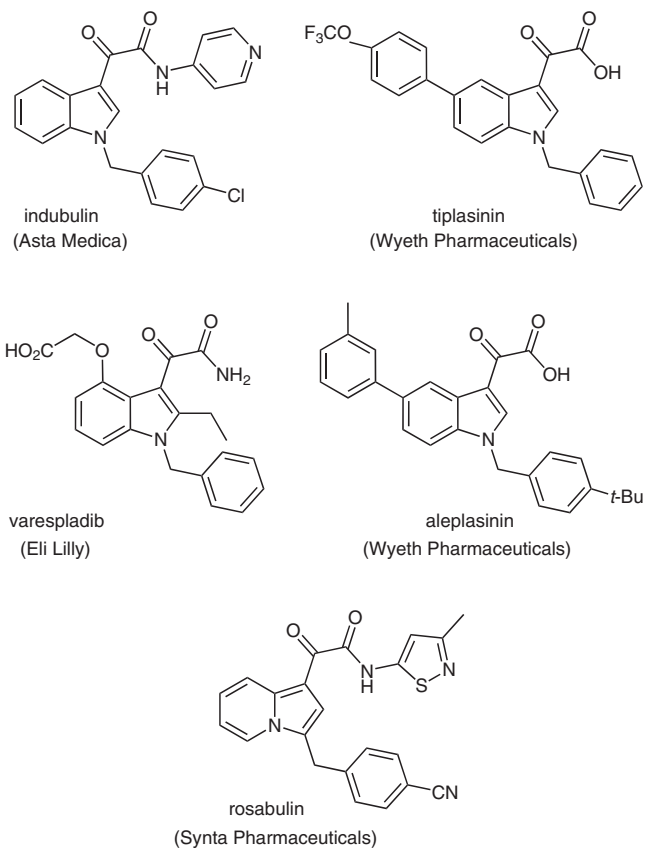


Figure 1 Examples of pharmacologically relevant heterocyclic α-keto acid derivatives: antineoplastics indibulin and rosabulin, antithrombotic tiplasinin, septic shock agent varespladib, and anti-Alzheimer's disease agent aleplasinin

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most probably gave the zwitterionic structure **B**, which underwent acyl transfer to afford the corresponding product **1a**. The structure of compound **1a** was proven by an X-ray diffraction study (Figure 2).

To demonstrate the applicability of the given transformation to form a wide variety of imidazoles, we performed several syntheses with diverse substrates **2**–**9** (Table 1). By following the elaborated protocol, the corresponding products **2a**–**9a** could be obtained in good to excellent yields of 85–95%.

With a practical procedure available for preparing 2-(2-ethoxy-1,2-dioxoethyl)imidazoles, we next carried out several experiments to find out whether this strategy could be applied to the synthesis of other 2-(2-ethoxy-1,2-dioxoethyl)azoles. The reaction of triazole **10** with ethyl oxalyl chloride under the standard reaction conditions resulted in the formation of a complex mixture. According to the LC-MS data, the mixture consisted mainly of compounds **10a**, **10b**, and **10c** (Scheme 2). The target product **10a** was isolated from the reaction mixture in 40% yield by distillation. Acidic hydrolysis of the residue obtained after distillation, i.e. crude compounds **10b** and **10c**, in aqueous hydrochloric acid provided the pure alcohol **10d** (Scheme 2).

The two thiazoles **11** and **12** were also tested (Table 1). The reactions of compounds **11** and **12** with ethyl oxalyl chloride by the standard protocol proceeded similarly to that of imidazole **10**, providing the corresponding products **11a** and **12a** in the moderate yields of 45% and 51%, respectively. Nevertheless, the formation of the side products was also observed.

Table 1 Synthesis of 2-(2-Ethoxy-1,2-dioxoethyl)azoles **1a**–**12a**

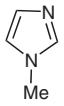
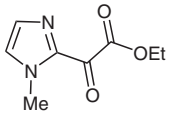
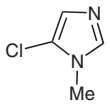
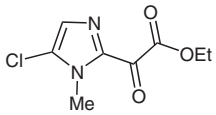
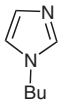
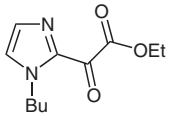
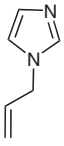
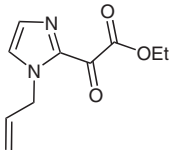
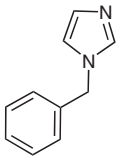
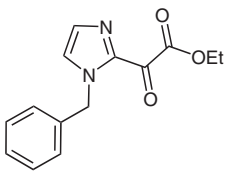
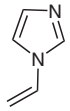
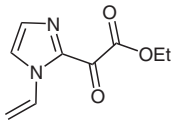
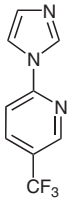
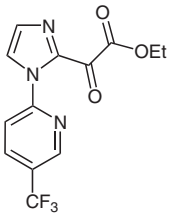
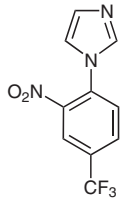
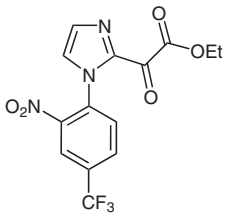
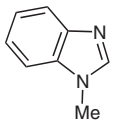
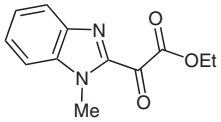
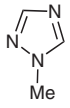
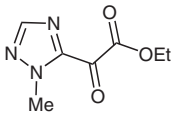
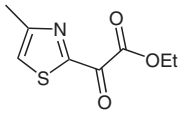
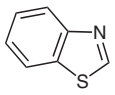
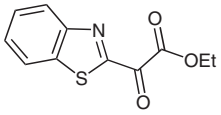
Azole	Product	Yield (%)
 **1**	 **1a**	95
 **2**	 **2a**	95
 **3**	 **3a**	85
 **4**	 **4a**	83

Table 1 Synthesis of 2-(2-Ethoxy-1,2-dioxoethyl)azoles **1a**–**12a** (continued)

Azole	Product	Yield (%)
 **5**	 **5a**	90
 **6**	 **6a**	85
 **7**	 **7a**	92
 **8**	 **8a**	85
 **9**	 **9a**	91
 **10**	 **10a**	40
 **11**	 **11a**	45
 **12**	 **12a**	51

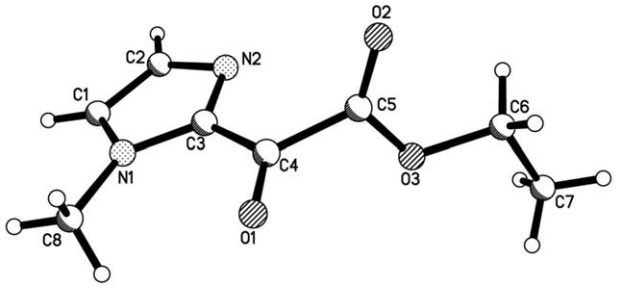
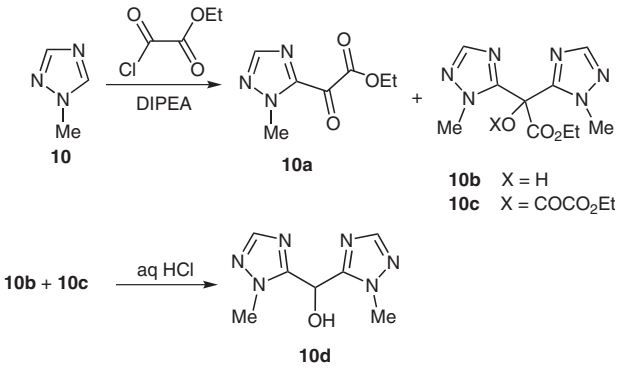


Figure 2 X-ray crystal structure of **1a**



Scheme 2 Synthesis of alcohol **10d**

Obviously, the activity of the carbonyl group in **1a**–**12a** and steric effects both influence the reaction yield significantly. The carbonyl groups in **10a**, **11a**, and **12a** are more active toward nucleophiles than those of compounds **1a**–**9a**, due to the strong electron-withdrawing nature of the triazole and thiazole moieties. Therefore, the products **10a**, **11a**, and **12a** can react with the corresponding intermediate **B** (Scheme 1), which results in the formation of the side products, thereby decreasing the yields of **10a**, **11a**, and **12a**, in contrast to the imidazole derivatives **1a**–**9a**.

In summary, we have shown that C-acylation of imidazoles with ethyl oxalyl chloride in the presence of *N*,*N*-diisopropylethylamine as a base is a facile and practical method for the preparation of 2-(2-ethoxy-1,2-dioxoethyl)imidazoles. To demonstrate the applicability of this strategy for the synthesis of other 2-(2-ethoxy-1,2-dioxoethyl)azoles, various model 2-(2-ethoxy-1,2-dioxoethyl)triazoles and 2-(2-ethoxy-1,2-dioxoethyl)thiazoles were prepared in 40–90% (non-optimized) yield. A systematic study on the C-acylation of various azoles with ethyl oxalyl chloride is ongoing.

^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance 500 spectrometer at 499.9, 124.9 and 470 MHz, respectively. Chemical shifts are reported in ppm downfield from TMS (^{1}H, ^{13}C) and C_6F_6 (^{19}F) as internal standard. Mass spectra (CI) were recorded on an Agilent 1100 LCMSD SL instrument.

Ethyl 2-Azolyl-2-oxoacetates 1a–13a; General Procedure

Ethyl oxalyl chloride (1.08 g, 0.01 mol) was added dropwise over 20 min to a stirred soln of the appropriate azole (0.01 mol) in CH_2Cl_2 (100 mL) at –20 °C. Then DIPEA (1.29 g, 0.01 mol) was added and the mixture was allowed to warm to r.t. The reaction mixture was stirred for an additional 12 h and then washed with H_2O (3 × 50 mL). The organic layer was dried (Na_2SO_4) and evaporated under vacuum to give the crude product.

Ethyl 2-(1-Methyl-1*H*-imidazol-2-yl)-2-oxoacetate (1a)

The crude product was purified by crystallization (*i*-PrOH–H_2O, 1:1).

Yield: 95%; colorless crystals; mp 48 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.55 (t, *J* = 7.0 Hz, 3 H), 3.19 (s, 3 H), 3.53 (q, *J* = 7.0 Hz, 2 H), 6.35 (s, 1 H), 6.73 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.01, 35.64, 62.39, 128.55, 131.88, 140.08, 163.75, 177.25.

MS (CI): *m*/*z* = 201 [M + 1 + H_2O].

Ethyl 2-(5-Chloro-1-methyl-1*H*-imidazol-2-yl)-2-oxoacetate (2a)

The crude product was purified by crystallization (*i*-PrOH).

Yield 95%; yellow powder; mp 45 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.31 (t, *J* = 7.1 Hz, 3 H), 3.93 (s, 3 H), 4.37 (q, *J* = 7.1 Hz, 3 H), 7.50 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.02, 32.60, 62.55, 127.15, 129.22, 139.48, 163.31, 176.75.

MS (CI): *m*/*z* = 217 [M + 1].

Ethyl 2-(1-Butyl-1*H*-imidazol-2-yl)-2-oxoacetate (3a)

The crude product was purified by flash column chromatography (silica gel, hexane–EtOAc, 4:1).

Yield 85%; brown liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.1 Hz, 3 H), 1.34–1.43 (m, 5 H), 1.76–1.82 (m, 2 H), 4.40 (t, *J* = 7.3 Hz, 2 H), 4.46 (q, *J* = 7.1 Hz, 2 H), 7.21 (s, 1 H), 7.30 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.51, 14.03, 19.62, 32.89, 48.30, 62.40, 127.46, 131.98, 139.62, 163.89, 177.35.

MS (CI): *m*/*z* = 225 [M + 1].

Ethyl 2-(1-Allyl-1*H*-imidazol-2-yl)-2-oxoacetate (4a)

The crude product was purified by flash column chromatography (silica gel, hexane–EtOAc, 4:1).

Yield 83%; brown liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.41 (t, *J* = 7.1 Hz, 3 H), 4.45 (q, *J* = 7.1 Hz, 2 H), 5.04 (m, 2 H), 5.17 (d, *J* = 16.9 Hz, 1 H), 5.28 (d, *J* = 10.7 Hz, 1 H), 5.96 (m, 1 H), 7.24 (s, 1 H), 7.33 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.03, 50.49, 62.47, 119.17, 120.88, 127.12, 130.89, 132.14, 136.02, 163.71, 177.35.

MS (CI): *m*/*z* = 227 [M + 1 + H_2O].

Ethyl 2-(1-Benzyl-1*H*-imidazol-2-yl)-2-oxoacetate (5a)

The crude product was purified by crystallization (*i*-PrOH).

Yield 90%; brown powder; mp 45 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.29 (t, *J* = 7.1 Hz, 3 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 5.64 (s, 2 H), 7.23 (d, *J* = 7.1 Hz, 2 H), 7.30–7.33 (m, 1 H), 7.36–7.40 (m, 3 H), 7.95 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.07, 51.66, 62.50, 127.34, 127.78, 127.95, 128.54, 129.07, 129.27, 132.32, 135.26, 139.75, 163.71, 177.56.

MS (CI): *m*/*z* = 259 [M + 1].

Ethyl 2-Oxo-2-(1-vinyl-1*H*-imidazol-2-yl)acetate (6a)
The crude product was purified by flash column chromatography (silica gel, hexane–EtOAc, 4:1).

Yield 85%; brown liquid.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.31 (t, *J* = 7.1 Hz, 3 H), 4.38 (q, *J* = 7.1 Hz, 2 H), 5.27 (d, *J* = 8.6 Hz, 1 H), 5.81 (d, *J* = 15.6 Hz, 1 H), 7.45 (s, 1 H), 7.77 (dd, *J* = 15.6, 8.6 Hz, 1 H), 8.29 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.36, 61.26, 103.57, 117.33, 127.52, 130.10, 136.56, 163.13, 176.30.

MS (CI): *m*/*z* = 213 [M + 1 + H_2O].

Ethyl 2-Oxo-2-{1-[5-(trifluoromethyl)-2-pyridyl]-1*H*-imidazol-2-yl}acetate (7a)
The crude product was purified by crystallization (*i*-PrOH).

Yield 92%; brown powder; mp 65 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.20 (t, *J* = 7.1 Hz, 3 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 7.53 (s, 1 H), 8.11 (d, *J* = 8.6 Hz, 1 H), 8.26 (s, 1 H), 8.59 (d, *J* = 8.6 Hz, 1 H), 8.98 (s 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.04, 62.78, 118.81, 126.13, 132.33, 138.10, 138.12, 140.79, 146.21, 146.24, 151.87, 162.38, 176.31.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –60.33.

MS (CI): *m*/*z* = 314 [M + 1].

Ethyl 2-{1-[2-Nitro-4-(trifluoromethyl)phenyl]-1*H*-imidazol-2-yl}-2-oxoacetate (8a)
The crude product was purified by crystallization (*i*-PrOH).

Yield 85%; brown powder; mp 116 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.32 (t, *J* = 7.1 Hz, 3 H), 4.40 (q, *J* = 7.1 Hz, 2 H), 7.63 (s, 1 H), 8.08 (s, 1 H), 8.11 (d, *J* = 8.1 Hz, 1 H), 8.41 (d, *J* = 8.1 Hz, 1 H), 8.69 (s, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.34, 62.89, 123.38, 123.41, 130.23, 132.06, 132.08, 132.15, 133.36, 134.12, 139.81, 145.35, 163.36, 176.91.

^{19}F NMR (470 MHz, DMSO-d_6): δ = –61.76.

MS (CI): *m*/*z* = 358 [M + 1].

Ethyl 2-(1-Methyl-1*H*-benzo[*d*]imidazol-2-yl)-2-oxoacetate (9a)
The crude product was purified by crystallization (*i*-PrOH).

Yield 91%; white powder; mp 103 °C.

^{1}H NMR (500 MHz, DMSO-d_6): δ = 1.35 (t, *J* = 7.1 Hz, 3 H), 4.15 (s, 3 H), 4.46 (q, *J* = 7.1 Hz, 2 H), 7.43 (t, *J* = 8.3 Hz, 1 H), 7.56 (t, *J* = 8.3 Hz, 1 H), 7.82 (d, *J* = 8.3 Hz, 1 H), 7.91 (d, *J* = 8.3 Hz, 1 H).

^{13}C NMR (125 MHz, DMSO-d_6): δ = 14.07, 31.89, 62.75, 110.61, 122.85, 124.38, 127.34, 137.07, 142.62, 142.97, 163.43, 180.45.

MS (CI): *m*/*z* = 251 [M + 1 + H_2O].

Ethyl 2-(1-Methyl-1*H*-1,2,4-triazol-5-yl)-2-oxoacetate (10a)
The crude product was purified by distillation (154–156 °C/3 Torr).

Yield 40%; colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7.1 Hz, 3 H), 4.16 (s, 3 H), 4.38 (q, *J* = 7.1 Hz, 2 H), 7.96 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.90, 36.13, 62.00 142.40, 145.20, 161.31, 183.27.

MS (CI): *m*/*z* = 201 [M + 1 + H_2O].

Bis(1-methyl-1*H*-1,2,4-triazol-5-yl)methanol (10d)
The residue left after the distillation of **10a**, namely a crude mixture of **10b** and **10c**, was suspended in MeOH (15 mL) and 10% aq HCl (15 mL). The reaction mixture was heated at reflux for 1 h. The solvent was removed under vacuum. The residue was triturated with acetone (30 mL), filtered, washed with acetone (30 mL), and dried under vacuum.

Yield 25%; white powder; mp 148 °C.

^{1}H NMR (500 MHz H_2O): δ = 3.8 (s, 6 H), 6.65 (s, 1 H), 8.20 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 36.92, 59.73, 146.68, 150.63.

MS (CI): *m*/*z* = 195 [M + 1].

Ethyl 2-(4-Methyl-1,3-thiazol-2-yl)-2-oxoacetate (11a)
The crude product was purified by distillation (117–121 °C/3 Torr).

Yield 45%; yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.26 (t, *J* = 7.1 Hz, 3 H), 2.44 (s, 3 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 6.94 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.04, 17.14, 62.91, 123.64, 157.02, 160.41, 162.48, 177.55.

MS (CI): *m*/*z* = 200 [M + 1].

Ethyl 2-(1,3-Benzothiazol-2-yl)-2-oxoacetate (12a)
The crude product was purified by flash column chromatography (silica gel, hexane–EtOAc, 4:1).

Yield 51%; yellow liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.48 (t, *J* = 7.2 Hz, 3 H), 4.56 (q, *J* = 7.2 Hz, 2 H), 7.62 (m, 2 H), 8.03 (d, *J* = 7.6 Hz, 1 H), 8.29 (d, *J* = 8.5 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.09, 63.09, 122.42, 126.39, 127.54, 128.78, 137.26, 153.59, 161.40, 162.44, 180.03.

MS (CI): *m*/*z* = 236 [M + 1].

X-ray Diffraction Structure of 1a
The crystals of **1a** ($C_8H_{10}N_2O_3$) are monoclinic. At 293 K, *a* = 8.0576(6), *b* = 13.8255(8), *c* = 8.3947(4) Å, *β* = 98.247(6)°, *V* = 925.5(1) Å^3, *Mr* = 182.18, *Z* = 4, space group $P2_1/c$, d_{calc} = 1.307 g/cm^3, μ(Mo Kα) = 0.102 mm^{-1}, *F*(000) = 384. Intensities of 8966 reflections (2703 independent, R_{int} = 0.029) were measured on an Xcalibur-3 diffractometer (graphite monochromated Mo Kα radiation, CCD detector, ω scanning, $2\Theta_{max}$ = 60°). The structure was solved by direct methods using the SHELXTL package.[9] The positions of the hydrogen atoms were located from electron density difference maps and refined by a riding model with U_{iso} = nU_{eq} (n = 1.5 for methyl groups and n = 1.2 for other hydrogen atoms) of the carrier atom. Restraints on the bond lengths of the ethyl group (1.54 Å) are used in the refinement of the structure. Full-matrix least-squares refinement against F^2 in the anisotropic approximation for non-hydrogen atoms using 2640 reflections was converged to wR_2 = 0.099 (R_1 = 0.042 for 1131 reflections with $F > 4\sigma(F)$, *S* = 0.753). CCDC 784044 contains the supplementary crystallographic data for **1a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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